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13. ABSTRACT (Maximum 200 words) Using theory and simulation, our goal was to: <ul style="list-style-type: none"> Determine the morphology of mixtures of nanoscopic rods and polymers Establish routes for driving nanoscopic spheres to self-assemble into rod-like or percolating structures within the polymers Predict the macroscopic properties of the reinforced polymers In order to carry out these studies, we employed hybrid models that we recently developed to investigate both the dynamic and equilibrium properties of nanocomposites. Our "CH/BD" model integrates a Cahn-Hilliard (CH) theory for binary blends with a Brownian dynamics (BD) simulation for nanoparticles to capture the structural evolution of the mixture. Our "SCF/DFT" combines a self-consistent field theory (SCFT) for diblock copolymers and density functional theory (DFT) for particles to generate the equilibrium morphology of the system. The structural information that we obtained from the CH/BD and SCF/DFT studies was then used to compute the mechanical, electrical or optical properties of the composite. In this manner, we could meet our goal of not only <i>characterizing the structure of the mixture</i> but also, determining the <i>macroscopic properties of those specific materials</i> . Such studies are vital for establishing fundamental structure-property relationships for nanocomposites.				
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Final Progress Report

Title: Modeling Polymers Containing Rod-Like Fillers: From Morphology to Mechanical Behavior
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Statement of the Problem Studied

Rod-like particles and fibers provide significant reinforcement of polymers and the resulting composites yield high-strength, lightweight materials. These materials can play a critical role in enhancing the fuel efficiency and durability of vehicles, and are vital in a broad range of infrastructure applications. Using theory and simulation, our goal was to:

- Determine the morphology of mixtures of nanoscopic rods and polymers
- Establish routes for driving nanoscopic spheres to self-assemble into rod-like or percolating structures within the polymers
- Predict the macroscopic properties of the reinforced polymers

Summary of the Most Important Results

In order to carry out these studies (1-15), we employed hybrid models that we recently developed to investigate both the dynamic and equilibrium properties of nanocomposites. Our “CH/BD” model integrates a Cahn-Hilliard (CH) theory for binary blends with a Brownian dynamics (BD) simulation for nanoparticles to capture the structural evolution of the mixture (1,8,15). Our “SCF/DFT” combines a self-consistent field theory (SCFT) for diblock copolymers and density functional theory (DFT) for particles to generate the equilibrium morphology of the system (2-5,7,9,11-14). The structural information that we obtained from the CH/BD and SCF/DFT studies was then used to compute the mechanical (1,5,8), electrical (1) or optical properties (2) of the composite. In this manner, we could meet our goal of not only *characterizing the structure of the mixture* but also, determining the *macroscopic properties of those specific materials*. Such studies are vital for establishing fundamental structure-property relationships for nanocomposites. Papers describing this research and acknowledging Army funding are marked with an asterisk at beginning of the Bibliography section of this proposal. The papers include two appearing in *Physical Review Letters* (4,11) and invited articles in *Current Opinion in Solid State and Materials Science* (7), *Composite Interfaces* (5) and *Molecular Simulations* (1). Below, we highlight some of our findings.

Using the CH/BD approach, we examined the dynamic behavior of a *binary polymer blend* that contains *nanoscale rods* (1). The incorporation of the nanorods into the minority phase of the phase-separating blend yielded a bicontinuous morphology, where the nanorods formed a percolating network within the continuous minority phase. This morphology served as the input to a lattice spring model (LSM), which was used to determine the mechanical properties, and a finite difference model (FDM), which was used to calculate the electrical conductance of the material (see Fig. 1 below). We found that in this doubly percolating system, the reinforcement efficiency of the nanorods and the electrical conductivity of the material are significantly increased relative to the

behavior in composites in which the nanorods are randomly dispersed in a homogeneous matrix. In particular, Fig. 1 shows that the rods give rise to significant strain reduction (as

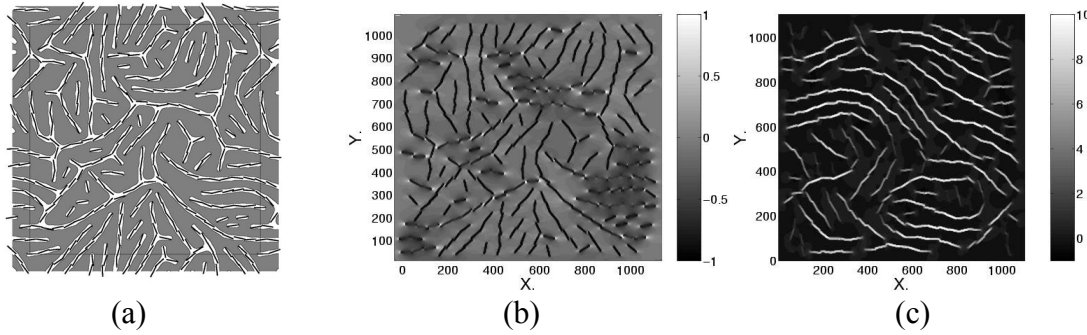
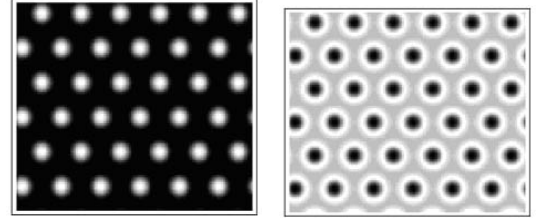


Fig. 1 (a) Morphology of nanorod/polymer blend system for a 6% volume fraction of nanorods. White regions are the minority phase A, gray regions are the majority phase B, and the rods are shown as black lines. (b) Normal strain field contours for a 6% nanorods in the phase-separating system. (c) Current density contours for 6% nanorods in the phase-separating system.

indicated by the dark regions in 1(b)) and thus, a stiffer material. The conducting rods also improve the conductance, as indicated by the white regions in 1(c). The integration of these various techniques allow us to predict the complex nanorod/polymer morphologies as a function of the constituents' characteristics, determine the mechanical and electrical behavior of the resultant material and consequently, relate the nanoscopic structure of the mixture to the macroscopic performance of the composite.

Using the SCF/DFT model, we recently undertook the first investigation into the rich behavior that emerges when *binary mixtures of large and small spheres* are blended with *AB microphase-separating copolymers* (9,11,12). We isolated an example of coupled self-assembly in such materials, where the system undergoes a nanoscale ordering of the spheres along with a phase transformation in the copolymer matrix. In particular, by replacing the 20% monodisperse *A*-like nanoparticles within the copolymer with a bidisperse mixture of 5% larger and 15% smaller particles, we could drive the system to undergo a transition from a lamellar structure to a cylindrical morphology. In addition, the larger particles are localized in the center of the *A* cylinders and the smaller particles form a corona around these larger species (as shown in Figure 2). The cylinders provide continuous reinforcement of the copolymer matrix. Furthermore, since the optical and electrical properties of semi-conductor and metallic particles are dependent on the particle size, the bidisperse particle mixture provides a means of fine-tuning the opto-electronic behavior of the system. It is noteworthy that our predictions on size-selective organization of binary particle mixtures in diblocks have recently been experimentally verified (16).

Fig. 2. SCF/DFT density profiles of nanoparticles within *AB* diblocks. The white regions mark the presence of a species while the black regions mark the absence of a species. The image on the left shows the distribution of the larger particles, which are localized in the center of the A domains. The image on the right displays the distribution of the smaller particles, which extend into the B matrix. A graded cylindrical morphology results from the introduction of the bidispersity.



We note that the observed self-assembly was driven by *entropic effects involving all the different components*. The results reveal that entropy can be exploited to create highly ordered nanocomposites with potentially unique electronic and photonic properties.

We also used the CH/BD model to determine the structural evolution of *spherical nanoparticles* in *symmetric diblocks* and compared the late-stage morphology of this mixture to the structure of randomly dispersed spheres in a homogeneous matrix (8). We found that the confinement of nanoparticles within a given domain of a bicontinuous diblock mesophase causes the particles to percolate and form essentially a rigid backbone

throughout the material at very low particle volume fractions, i.e., at roughly ten percent. On the other hand, the percolation threshold for particles in a homogeneous matrix in 3D is roughly 22 percent (15). We then mapped the different morphologies onto the LSM lattice to establish how the spatial distribution of these particles affects the mechanical behavior of the composite. In particular, we applied a stress in the simulation and calculated the local strain fields and overall elastic response of the different materials. We found that the continuous distribution of fillers significantly increases the reinforcement efficiency of the nanoparticles and dramatically increases the Young's modulus of the material, as shown in Fig. 3. The value of Γ in the figure characterizes the width of the diblock domains. By integrating these morphological and mechanical models, we could determine how modifications in physical characteristics of the particles and diblocks affect both the structure of the mixture and

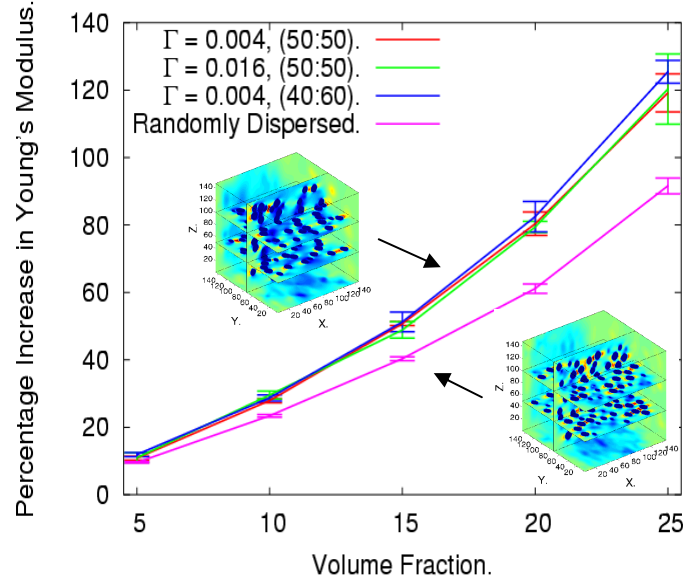


Fig. 3. Percentage increases in Young's moduli vs. particle volume fraction for the cases where the particles are confined in diblocks (upper curves) and randomly dispersed in a homogeneous (homopolymer) matrix. The images display the local strains in the materials, with the upper image being for a copolymer/particle system and the lower image being for a homopolymer/particle mixture

the behavior of the material.

In summary, the results of these studies can ultimately aid researchers in understanding how choices made in the nature of the components affect the performance of the final product. The techniques and studies described above provide a useful foundation for the proposed research and give us a unique advantage in being able to carry out the new studies.

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(a) Papers published in peer-reviewed journals

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Book Chapter

- (1) Buxton, G.A. and Balazs, A.C. "Supramolecular Networks Synthesized in Nanoparticle-Polymer Mixtures", in Encyclopedia of Nanoscience and Nanotechnology, James A. Schwarz, Cristian I. Contescu, and Karol Putyera, Eds.; Marcel Dekker, Inc.: New York, 2004; pp 3785-3794.

(b) Papers published in non peer-reviewed journals or conference proceedings—0

(c) Papers presented at meetings but not published in conference proceedings
Presentations were made each year at the APS, ACS, MRS meetings.

(d) Manuscripts submitted, but not published

- (1) Balazs, A.C. and Buxton, G. A., "Modeling the Structural Evolution, Equilibrium Morphology and Macroscopic Behavior of Polymer/Nanoparticle Composites", Handbook of Theoretical And Computational Nanotechnology, American Scientific Publishers, in press.

(e) Technical reports submitted to ARO—0

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